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Influence of temperature on the volumetric properties of ethanol + water + 1–pentanol

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Abstract: Knowledge of physical properties and phase equilibria is necessary for the design and optimization of the equipment for the production of distilled alcoholic beverages. In this paper the temperature dependence of the excess molar volumes of the ternary system ethanol + water + 1-pentanol in the temperature range 228.15 – 323.15 K and atmospheric pressure, are presented, due to the importance of 1-pentanol among the flavour compounds contained in this type of beverages. The excess molar volumes are negative over the whole homogeneous composition range, but tend to positive values towards the binaries ethanol + 1-pentanol and water + 1-pentanol. Because the design of current processes is strongly computer oriented, consideration was also given to how accurate the predictions of the SRK equations of state are. Different derived properties were computed due to their importance in the study of specific molecular interactions.

Keywords: excess molar volume, temperature, ethanol, water, 1-pentanol, prediction.

INTRODUCTION

Knowledge of the thermodynamic properties and phase equilibria of ethanol, water and the different flavour components in distilled alcoholic beverages is of practical interest to the food technology since the applied industrial procedures are closely related to their temperature and pressure dependence. In accordance to this, in the last few years, a considerable effort has developed in the field of thermodynamic properties although a great scarcity of data is observed in the open literature for mixtures present in alcoholic beverages. Such properties are strongly dependent on the hydrogen-bond potential of hydroxyl groups, chain length and isomeric structures, as well as the molecular packing. Due to the different origin of the grapes, thermal conditions of the fermentation chemical reactions and the com-

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plexity of the composition and molecular chains of the components, currently a considerable lack of accuracy and thermodynamic consistency in the available open literature data can be observed. Simulation and optimization are not used in a proper manner in this matter, an overestimation of the equipment or high energy-consuming conditions usually being applied due to inaccurate calculations. The difficulties encountered in simulation in these types of processes have been commented upon previously.[1] With the scope of investigations of the physical properties related to equipment design of distilled alcoholic beverages processes, as well as energy optimization and quality and flavouring ensurement, the temperature dependence of the excess molar volumes of the ethanol + water + 1-pentanol system in the temperature range 288.15 – 323.15 K at atmospheric pressure as a function of the molar composition is presented in this paper, as a continuation of previous papers. The experimental heterogeneous region has been studied previously as a function of temperature,[2] hence only the volumetric trend of the homogeneous region is encompassed in this study. From the experimental values, the excess molar volumes were computed and a temperature dependent Cibulka type polynomial fitted to the results.[3] On the basis of the experimental measurements of such data and the fact that current process design is strongly computer oriented, consideration was also given to the applicability of the SRK equation of state. Previously published data of the binary mixtures encompassed in the studied ternary mixture were used to calculate the Soave–Redlich–Kwong (SRK)[4] binary interaction parameters for prediction of the ternary trend. The temperature and functional dependence of the partial molar quantities, excess isobaric expansibility and isothermal coefficient of pressure excess molar enthalpy are analyzed and commented upon in terms of steric hindrance and molecular interactions. The use of binary interaction parameters of cubic equations of state was shown to be a simple and accurate procedure[5] to predict multicomponent excess trends and compute the derived multicomponent excess functions of different thermodynamic magnitudes, but their applicability to mixtures of intense interaction and partial miscibility may be severely limited if the ternary contribution is considerable, as in this case.

EXPERIMENTAL

All chemical solvents used in the preparation of samples were of Merck quality with purity better than 99.5 mol%. The pure components were stored in the dark at constant humidity and temperature. In order to reduce errors in the mole fraction, the vapour space in the vessels was minimized during preparation of the samples. Mixtures were prepared by mass using a Salter ER-182A balance, the whole composition range of the ternary mixture being covered. The obtained accuracy in molar fractions was higher than $\pm 5 \times 10^{-4}$. The densities of the pure components and their mixtures were measured with an Anton Paar DSA-48 vibrational tube densimeter and sound analyzer, with a resolution of 10^{-5} g cm^{-3} and 1 ms^{-1}. The apparatus was calibrated periodically in accordance with the vendor instructions using a double reference (Millipore quality water and ambient air at each temperature). The accuracy in the calculation of the excess molar volumes was estimated to be better than $\pm 2\times10^{-2}$ cm^3 mol^{-1} and the temperature of the measurement to $\pm 10^{-2}$ K. The experimental and literature densities of the solvents are given in Table I. More details about the employed techniques and procedures can be obtained from a previously published work.[6]

TABLE I. Comparison of the experimental density (g cm^{-3}) with literature data for the employed chemicals at the studied temperatures

Component	Molecular weight	288.15 K	290.65 K	293.15 K	295.65 K	298.15 K	300.65 K	303.15 K	305.65 K	308.15 K	310.65 K	313.15 K	315.65 K	318.15 K	320.65 K	323.15 K	lit. (298.15 K)(a)
Ethanol	46.070	0.79444	0.79230	0.79016	0.78803	0.78589	0.78373	0.78159	0.77940	0.77724	0.77285	0.77062	0.76848	0.76620	0.76402	0.77505	0.78493 0.78730[b]
Water	18.015	0.99910	0.99868	0.99820	0.99765	0.99704	0.99637	0.99565	0.99486	0.99403	0.99221	0.99124	0.99021	0.98915	0.98804	0.99315	0.99705 0.99712[b]
1-Pentanol	88.149	0.81813	0.81637	0.81456	0.81273	0.81091	0.80907	0.80723	0.80537	0.80352	0.80164	0.79974	0.79785	0.79604	0.79407	0.79225	0.81080

(a) Ref. 10

(b) Ref. 11

DATA CORRELATION

The excess molar volumes of the ternary mixture were computed applying the following eqauation:

$$V^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \tag{1}$$

where ρ is the density of the mixture, ρ_i the density of the pure component i, and x_i is the molar fraction of i. N is the number of components in the mixture. The densities of the mixture and excess molar volumes are given in Table II as a function of temperature. The computed excess molar volumes of the binary mixtures were fitted using a temperature dependent Cibulka expression.[3] This equation was used to correlate the ternary derived properties of the mixtures, by using the unweighted least squares method, *i.e.* all experimental points were weighted equally. The necessary binary fitting parameters of the encompassed binary mixtures were computed in a previous paper.[4] The parameters were calculated using a non-linear optimization algorithm according to Marquardt.[7] The ternary derived magnitudes were fitted to the equation:

$$\Delta Q_{123} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} + \Delta_{123} \tag{2}$$

where the binary magnitudes ΔQ_{ij} were correlated by means of the Redlich-Kister equation.[8] (Eq. (3))

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^{S} \left(\sum_{q=0}^{U} A_{pq} T^q \right) (x_i - x_j)^p \tag{3}$$

and Δ_{123}, the ternary contribution was fitted by means of Eq. (4). ΔQ_{ij} is the excess property, A_{pq} are the temperature dependent parameters for the binary mixtures and T is the absolute temperature. These parameters were obtained by the unweighted least squares method applying a fitting algorithm as commented above. S and U are the degrees of the polynomial expansion, which were optimized by means of the Bevington test.[9] In order to obtain generalized parameters, a temperature polynomial expansion was applied.

$$\Delta_{123} = x_1 x_2 x_3 RT(B_0 + B_1 x_1 + B_2 x_2) \tag{4}$$

where R is the universal gas constant. Every B_i ternary parameter is a function of temperature as expressed in Eq. (5)

$$B_i = \sum_{q=0}^{W} C_{iq} T^q \tag{5}$$

The values W, the limit of expansion of the series, were selected in order to minimize the root mean square deviations. The ternary parameters of Eq. (5) and the corresponding root mean square deviations are given in Table III. The root mean square deviations were computed using Eq. (6), where z is the value of the excess property, and n_{DAT} is the number of experimental data points.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} \left(z_{\exp} - z_{\mathrm{cal}} \right)^2}{n_{DAT}} \right)^{1/2} \tag{6}$$

We are not aware of the existence of the physical property data of this system in the earlier literature. The excess molar volumes of each ternary mixture at 298.15 K as a function of molar fractino are shown in Fig. 1. This system shows a negative trend at all experimental compositions and temperatures. A slight decrease of this trend (expansive behaviour) is shown towards the binaries ethanol + 1-pentanol or water + 1-pentanol.[4] Only expansion is observed in the vicinity of these binaries due to packing difficulties of the polar molecules among the aliphatic end of 1-pentanol. Not surprisingly, the lowest excess molar volumes were exhibited by the binary mixture ethanol + water, this effect being smaller as

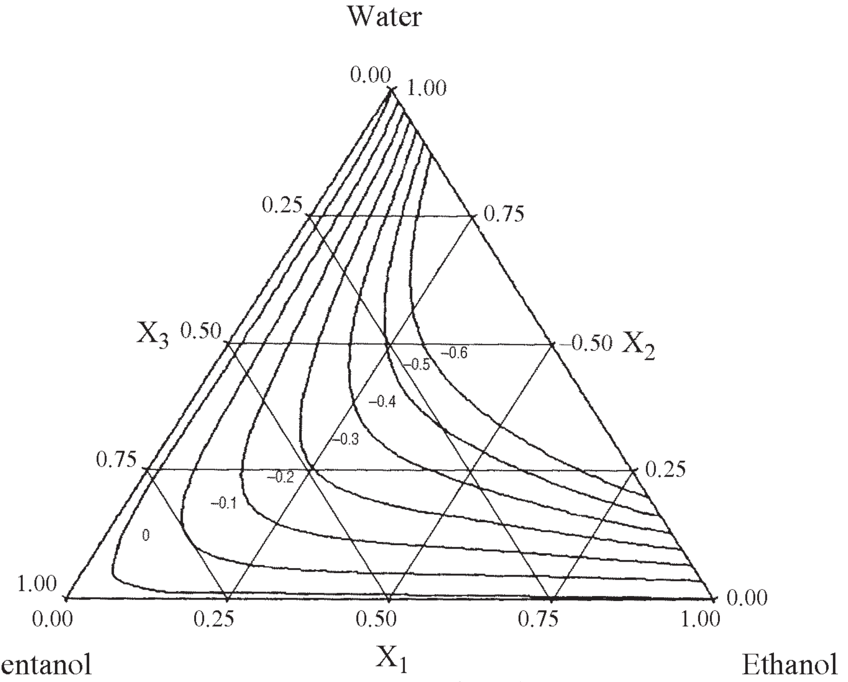

FIG. 1. Curves of constant excess molar volumes (cm^3 mol^{-1}), attaining to the Cibulka equation (Eqs. 2 and 4), of ethanol (1) + water (2) + 1-pentanol (3) at 298.15 K.

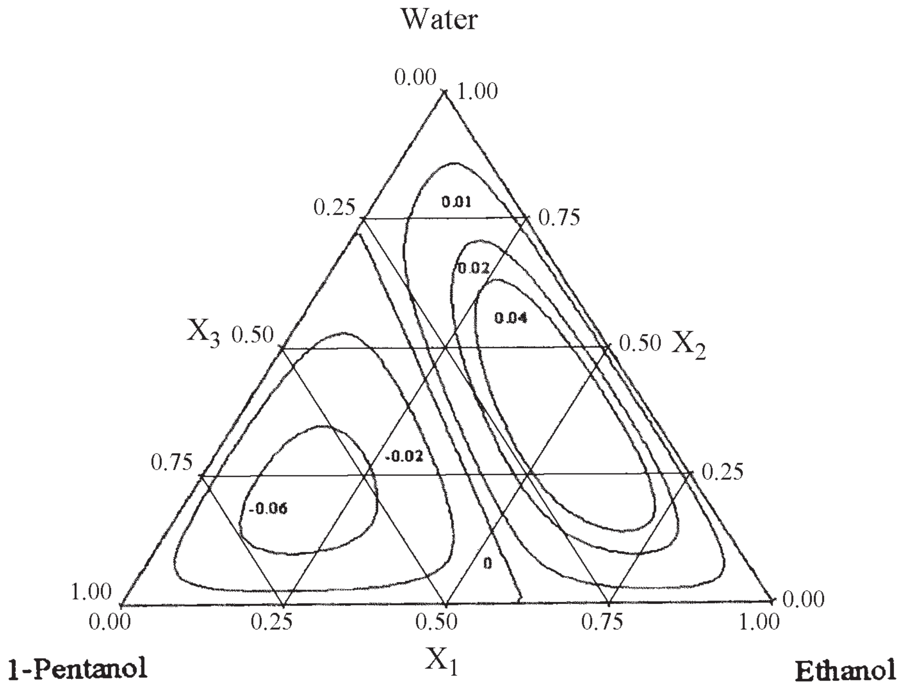

FIG. 2. Curves of constant ternary contribution to the excess molar volumes (Eq. (4)) of ethanol (1) + water (2) + 1-pentanol (3) at 298.15 K.

the temperature increases, due to diminishing potential of H-bond formation. A fact to be pointed out is the huge ternary contribution exibited at high concentrations of 1-pentanol (80 % of the total value). The ternary contribution is expressed in accordance to the Cibulka equation as calculated using Eq. (4). The results are shown in Fig. 2, from which two clearly differing trends can be seen a huge negative tendency when the concentrations of ethanol and water are small and slight positive near the binary ethanol + water due to the non-tolerance of the aliphatic end of the large alcohol in the neighboutrhood of this binary mixture. This positive contribution of the ternary part increases with increasing temperature due to dispersive forces among the aliphatic ends.

DERIVED PROPERTIES

A frequently applied derived magnitude for industrial mixtures is the temperature dependence of volumetry, which is expressed as the isobaric expansibility or thermal expansion coefficient (α). The data reported in the literature usually give only values of thermal expansion coefficients of both pure compounds and their mixtures, showing the relative changes in the density, calculated by means of ($-\Delta\rho/\rho$) as a function of temperature and assuming that α remains constant in any thermal range. As in the case of pure chemicals, a molar fraction can be computed using the expression:

$$\alpha = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{P,x} \tag{7}$$

which takes into account the temperature dependence of the density. However a more interesting contribution is made to the field of properties in liquid mixtures if this calculation is done taking separately the partial contributions of the thermal expansibilities of each component in the mixture, as well as that due to non-idealiy in the mixture. To this aim, the basic expression of the excess thermal expansion is as follows.[6]

$$\alpha^{\mathrm{E}} = \alpha - \sum_{i=1}^{N} \varphi_i \alpha_i \tag{8}$$

where

$$\varphi_i = \frac{x_i V_i}{\sum_{i=1}^{N} x_i V_i} \tag{9}$$

where φ_i is the volume fraction of the components in the mixture; this propery can be described as the variation of density with respect to the property at such a condition with temperature due to the non-ideality of the mixture. The values of the excess isobaric expansibility computed from the measured densities are also given in Table II. The excess isobaric expansibility of the ternary mixture is shown in Fig. 3. This Figure expresses the excess magnitude as a function of $z = \prod_i x_i$. For this system, it is convenient to present the α^{E} and $(\partial H/\partial P)_{T,x}$ *vs.* z (Figs. 3 and 4 of the

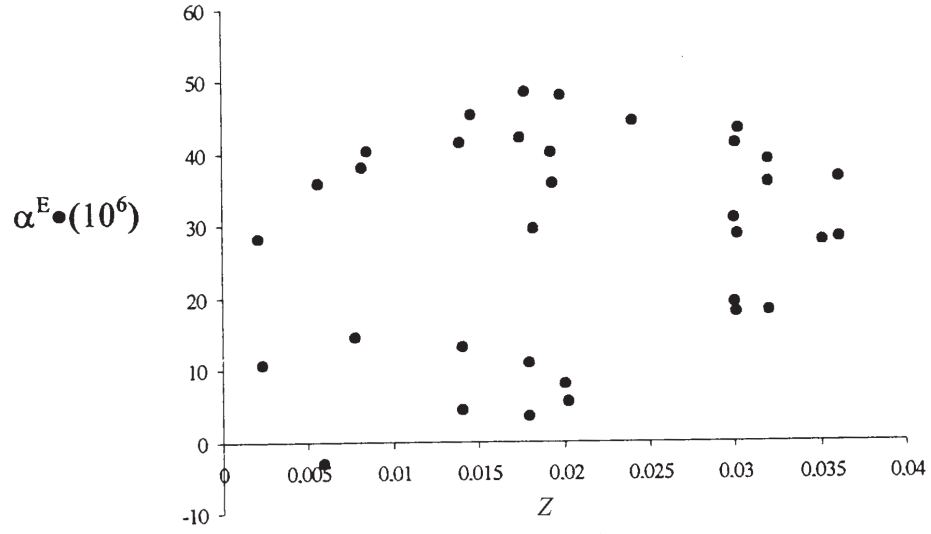

Fig. 3. Curves of constant excess isobaric expansibility (α^{E} K^{-1}) as a function of z for ethanol (1) + water (2) + 1-pentanol (3) at 298.15 K.

manuscript) in an alternative form; namely, the quantity *z* could be replaced by the molar fraction *x*. This procedure is a simple way to visualise ternary representations in an-*xy* diagram. In Fig. 3 two indicative facts are observed: first the influence of temperature, which changes the negative values for the highest temperature towards positive values at the lowest one, secondly, a clear increasing tendency towards the binary water + 1-pentanol system can be observed.

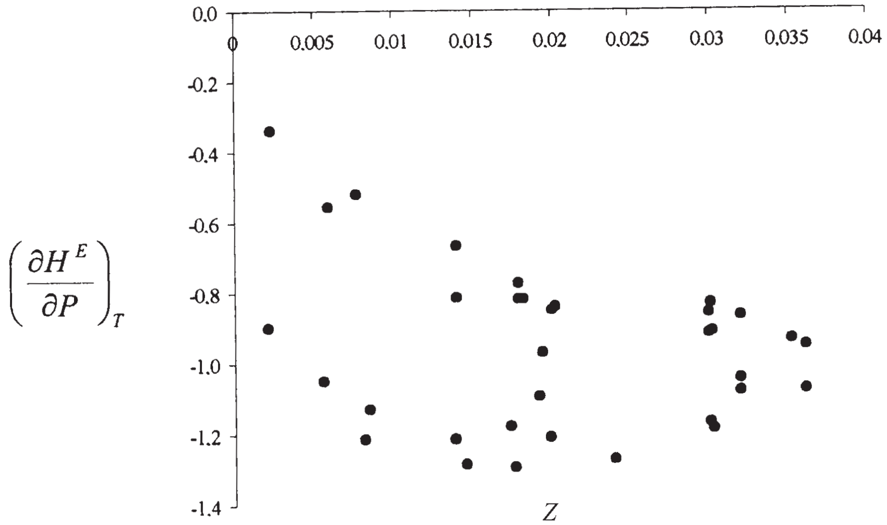

Fig. 4. Curves of constant isothermal coefficient of pressure excess molar enthalpy ($\partial H^E/\partial P$) (J M Pa^{-1} mol^{-1}) as a function of *z* for ethanol (1) + water (2) + 1-pentanol (3) at 298.15 K.

The isothermal coefficient of pressure excess molar enthalpy can be derived accurately from volumetric measurements by application of the following expression:

$$\left(\frac{\partial H^{\mathrm{E}}}{\partial P}\right)_{T,x} = V^{\mathrm{E}} - T\left(\frac{\partial V^{\mathrm{E}}}{\partial T}\right)_{P,x} \tag{10}$$

This magnitude stands for the dependence of the excess molar enthalpy of mixing with pressure at a fixed composition and temperature. This magnitude exhibitis an inversion of sign as a function of composition for the higher temperatures, gathering negative values in the other cases. In terms of composition, the proximity of the binodal curve near 1-pentanol shows the lowest values of the isothermal coefficient of pressure excess molar enthalpy.

Partial molar quantities are important in the study of the dependence of an extensive property on phase composition at a constant pressure and temperature, a trend being shown with composition. The partial excess molar volume of a component in a multicomponent mixture can be computed from excess molar volume data by means of:

TABLE II. Densities (*r*), excess molar volumes (V^{E}), excess isobaric expansibilities (a$^{\mathrm{E}}$) and isothermal pressure dependence of excess molar enthalpies ((¶H^{E}/¶P)$_T$) on mixing for the mixture ethanol (1) + water (2) + 1-pentanol (3) at different temperatures

x_1	x_2	ρ (g cm^{-3})	V^{E} (cm^3 mol^{-1})	$10^6\alpha^{\mathrm{E}}$ (K^{-1})	$(\partial H^{\mathrm{E}}/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^{E} (cm^3 mol^{-1})	$10^6\,\alpha^{\mathrm{E}}$ (K^{-1})	$(\partial H^{\mathrm{E}}/\partial P)_T$ (JMPa^{-1} mol^{-1})
323.15 K											
0.8981	0.0523	0.77185	–0.136	–14.582	0.148	0.3000	0.3014	0.80376	–0.270	–17.932	0.108
0.0498	0.0458	0.79312	–0.015	–12.866	0.393	0.2871	0.4241	0.81553	–0.375	–23.664	0.047
0.8037	0.0947	0.77842	–0.231	–20.302	0.169	0.2992	0.4993	0.82605	–0.487	–28.969	–0.038
0.6996	0.2006	0.79209	–0.588	–25.036	–0.136	0.3007	0.6001	0.84674	–0.655	–31.996	–0.254
0.6014	0.2984	0.80200	–0.590	–28.884	–0.107	0.2009	0.0988	0.79293	–0.066	–8.185	0.156
0.5974	0.1010	0.78489	–0.167	–22.359	0.339	0.2008	0.1996	0.79795	–0.124	–7.192	0.048
0.5014	0.3983	0.81512	–0.668	–31.923	–0.179	0.2031	0.3003	0.80408	–0.170	–9.042	0.025
0.5005	0.3000	0.80238	–0.457	–30.092	0.093	0.1995	0.4009	0.81268	–0.260	–12.535	–0.019
0.4983	0.2017	0.79378	–0.291	–24.967	0.238	0.2003	0.5006	0.82388	–0.337	–17.926	–0.037
0.5012	0.0963	0.78696	–0.131	–18.856	0.324	0.1999	0.7001	0.86567	–0.554	–26.535	–0.258
0.4010	0.0955	0.78904	–0.100	–14.709	0.274	0.1004	0.1029	0.79499	–0.086	–6.912	0.106
0.4002	0.1992	0.79518	–0.229	–19.719	0.218	0.1032	0.2046	0.79909	–0.050	–1.821	–0.021
0.3986	0.3022	0.80319	–0.357	–25.601	0.148	0.0986	0.3001	0.80476	–0.094	0.570	–0.130
0.4010	0.3988	0.81366	–0.503	–30.921	0.020	0.0994	0.3996	0.81214	–0.142	0.075	–0.164
0.4005	0.4981	0.82979	–0.693	–33.309	–0.227	0.1479	0.0469	0.79142	–0.002	–10.200	0.302
0.3026	0.0958	0.79098	–0.079	–10.978	0.211	0.2520	0.0482	0.78961	–0.011	–9.955	0.271
0.2968	0.2023	0.79682	–0.170	–13.292	0.144	0.1500	0.8005	0.89779	–0.473	–20.423	0.287
320.65 K											
0.8981	0.0523	0.77399	–0.136	–12.107	0.097	0.3000	0.3014	0.80578	–0.280	–12.590	–0.019
0.0498	0.0458	0.79500	–0.022	–8.826	0.252	0.2871	0.4241	0.81756	–0.385	–18.616	–0.057
0.8037	0.0947	0.78055	–0.232	–16.895	0.097	0.2992	0.4993	0.82810	–0.496	–24.283	–0.121

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
0.6996	0.2006	0.79420	–0.588	–21.312	–0.208	0.3007	0.6001	0.84879	–0.661	–28.520	–0.307
0.6014	0.2984	0.80416	–0.596	–25.010	–0.182	0.2009	0.0988	0.79486	–0.073	–3.308	0.007
0.5974	0.1010	0.78694	–0.171	–17.269	0.215	0.2008	0.1996	0.79990	–0.134	–2.134	–0.094
0.5014	0.3983	0.81728	–0.675	–28.023	–0.250	0.2031	0.3003	0.80606	–0.182	–3.901	–0.105
0.5005	0.3000	0.80449	–0.465	–25.271	–0.008	0.1995	0.4009	0.81467	–0.271	–7.468	–0.133
0.4983	0.2017	0.79584	–0.298	–19.711	0.115	0.2003	0.5006	0.82586	–0.345	–13.129	–0.129
0.5012	0.0963	0.78896	–0.135	–13.493	0.187	0.1999	0.7001	0.86761	–0.560	–23.506	–0.299
0.4010	0.0955	0.79102	–0.105	–9.325	0.127	0.1004	0.1029	0.79688	–0.092	–2.480	–0.035
0.4002	0.1992	0.79719	–0.236	–14.280	0.082	0.1032	0.2046	0.80102	–0.061	2.801	–0.157
0.3986	0.3022	0.80525	–0.367	–20.334	0.030	0.0986	0.3001	0.80668	–0.104	5.271	–0.254
0.4010	0.3988	0.81574	–0.511	–26.136	–0.073	0.0994	0.3996	0.81408	–0.153	4.794	–0.275
0.4005	0.4981	0.83191	–0.699	–29.518	–0.291	0.1479	0.0469	0.79330	–0.006	–5.677	0.156
0.3026	0.0958	0.79293	–0.085	–5.769	0.061	0.2520	0.0482	0.79149	–0.012	–5.013	0.123
0.2968	0.2023	0.79879	–0.179	–7.945	0.004	0.1500	0.8005	0.89961	–0.531	–18.720	–0.362
318.15 K											
0.8981	0.0523	0.77185	–0.137	–9.620	0.046	0.3000	0.3014	0.80376	–0.290	–7.224	–0.144
0.0498	0.0458	0.79312	–0.024	–4.771	0.117	0.2871	0.4241	0.81553	–0.396	–13.548	–0.160
0.8037	0.0947	0.77842	–0.235	–13.473	0.024	0.2992	0.4993	0.82605	–0.506	–19.779	–0.205
0.6996	0.2006	0.79209	–0.589	–17.571	–0.279	0.3007	0.6001	0.84674	–0.670	–25.032	–0.361
0.6014	0.2984	0.80200	–0.603	–21.118	–0.257	0.2009	0.0988	0.79294	–0.077	1.590	–0.136
0.5974	0.1010	0.78489	–0.174	–12.156	0.094	0.2008	0.1996	0.79795	–0.143	2.947	–0.233
0.5014	0.3983	0.81512	–0.682	–24.105	–0.320	0.2031	0.3003	0.80408	–0.193	1.262	–0.233
0.5005	0.3000	0.80238	–0.473	–20.429	–0.107	0.1995	0.4009	0.81268	–0.282	–2.379	–0.245

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\ \alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
0.4983	0.2017	0.79378	–0.304	–14.430	–0.006	0.2003	0.5006	0.82388	–0.356	–8.313	–0.222
0.5012	0.0963	0.78696	–0.139	–8.106	0.050	0.1999	0.7001	0.86567	–0.567	–20.467	–0.342
0.4010	0.0955	0.78904	–0.109	–3.918	–0.017	0.1004	0.1029	0.79499	–0.098	1.970	–0.174
0.4002	0.1992	0.79518	–0.244	–8.816	–0.051	0.1032	0.2046	0.79909	–0.070	7.442	–0.289
0.3986	0.3022	0.80319	–0.375	–15.042	–0.085	0.0986	0.3001	0.80476	–0.116	9.992	–0.377
0.4010	0.3988	0.81366	–0.521	–21.332	–0.167	0.0994	0.3996	0.81214	–0.164	9.534	–0.385
0.4005	0.4981	0.82979	–0.708	–25.712	–0.355	0.1479	0.0469	0.79142	–0.008	–1.136	0.014
0.3026	0.0958	0.79098	–0.089	–0.537	–0.086	0.2520	0.0482	0.78961	–0.014	–0.051	–0.025
0.2968	0.2023	0.79682	–0.187	–2.575	–0.135	0.1500	0.8005	0.89779	–0.536	–17.013	–0.384
315.65 K											
0.8981	0.0523	0.77185	–0.139	–7.117	–0.004	0.3000	0.3014	0.80376	–0.299	–1.831	–0.267
0.0498	0.0458	0.79312	–0.027	–0.698	–0.016	0.2871	0.4241	0.81553	–0.406	–8.451	–0.261
0.8037	0.0947	0.77842	–0.238	–10.028	–0.047	0.2992	0.4993	0.82605	–0.514	–15.147	–0.286
0.6996	0.2006	0.79209	–0.590	–13.807	–0.348	0.3007	0.6001	0.84674	–0.677	–21.520	–0.414
0.6014	0.2984	0.80200	–0.610	–17.200	–0.331	0.2009	0.0988	0.79294	–0.081	6.509	–0.277
0.5974	0.1010	0.78489	–0.178	–7.014	–0.025	0.2008	0.1996	0.79795	–0.151	8.051	–0.368
0.5014	0.3983	0.81512	–0.689	–20.161	–0.388	0.2031	0.3003	0.80408	–0.203	6.449	–0.358
0.5005	0.3000	0.80238	–0.483	–15.557	–0.207	0.195	0.4009	0.81268	–0.293	2.734	–0.355
0.4983	0.2017	0.79378	–0.312	–9.120	–0.125	0.2003	0.5006	0.82388	–0.365	–3.473	–0.312
0.5012	0.0963	0.78696	–0.143	–2.692	–0.084	0.1999	0.7001	0.86567	–0.573	–17.409	–0.383
0.4010	0.0955	0.78904	–0.114	1.515	–0.159	0.1004	0.1029	0.79499	–0.104	6.438	–0.310
0.4002	0.1992	0.79518	–0.251	–3.324	–0.182	0.1032	0.2046	0.79909	–0.081	12.102	–0.420
0.3986	0.3022	0.80319	–0.383	–9.720	–0.198	0.0986	0.3001	0.80476	0.052	14.732	–0.319

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
0.4010	0.3988	0.81366	–0.529	–16,498	–0.258	0.0994	0.3996	0.81214	–0.021	14.292	–0.338
0.4005	0.4981	0.82979	–0.715	–21.881	–0.418	0.1479	0.0469	0.79142	0.227	3.424	0.110
0.3026	0.0958	0.79098	–0.092	4.718	–0.229	0.2520	0.0482	0.78961	0.210	4.932	0.056
0.2968	0.2023	0.79682	–0.194	2.821	–0.270	0.1500	0.8005	0.89779	–0.488	–15.296	–0.351
313.15K											
0.8981	0.0523	0.77185	–0.140	–4.600	–0.054	0.3000	0.3014	0.80376	–0.309	3.588	–0.389
0.0498	0.0458	0.79312	–0.033	3.389	–0.150	0.2871	0.4241	0.81553	–0.416	–3.331	–0.361
0.8037	0.0947	0.77841	–0.241	–6.566	–0.117	0.2992	0.4993	0.82605	–0.524	–10.494	–0.368
0.6996	0.2006	0.79209	–0.592	–10.024	–0.418	0.3007	0.6001	0.84674	–0.685	–17.992	–0.466
0.6014	0.2984	0.80200	–0.617	–13.261	–0.403	0.2009	0.0988	0.79294	–0.088	11.449	–0.420
0.5974	0.1010	0.78489	–0.183	–1.848	–0.145	0.2008	0.1996	0.79795	–0.162	13.177	–0.504
0.5014	0.3983	0.81512	–0.696	–16.198	–0.457	0.2031	0.3003	0.80408	–0.214	11.660	–0.483
0.5005	0.3000	0.80238	–0.491	–10.661	–0.304	0.1995	0.4009	0.81268	–0.304	7.871	–0.464
0.4983	0.2017	0.79378	–0.319	–3.784	–0.243	0.2003	0.5006	0.82388	–0.376	1.389	–0.404
0.5012	0.0963	0.78696	–0.149	2.749	–0.218	0.1999	0.7001	0.86567	–0.580	–14.339	–0.424
0.4010	0.0955	0.78904	–0.119	6.973	–0.300	0.1004	0.1029	0.79499	–0.114	10.923	–0.448
0.4002	0.1992	0.79518	–0.259	2.195	–0.312	0.1032	0.2046	0.79909	–0.090	16.783	–0.549
0.3986	0.3022	0.80319	–0.393	–4.384	–0.312	0.0986	0.3001	0.80476	–0.139	19.493	–0.618
0.4010	0.3988	0.81366	–0.538	–11.641	–0.348	0.0994	0.3996	0.81214	–0.188	19.072	–0.601
0.4005	0.4981	0.82979	–0.723	–18.030	–0.480	0.1479	0.0469	0.79142	–0.014	8.003	–0.267
0.3026	0.0958	0.79098	–0.099	9.997	–0.373	0.2520	0.0482	0.78961	–0.20	9.937	–0.315
0.2968	0.2023	0.79682	–0.204	8.241	–0.406	0.1500	0.8005	0.89779	–0.546	–13.572	–0.426

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
310.65 K											
0.8981	0.0523	0.77185	–0.142	–2.070	–0.104	0.3000	0.3014	0.80376	–0.319	9.032	–0.508
0.0498	0.0458	0.79312	–0.036	7.493	–0.279	0.2871	0.4241	0.81553	–0.427	1.814	–0.460
0.8037	0.0947	0.77842	–0.245	–3.084	–0.187	0.2992	0.4993	0.82605	–0.534	–5.817	–0.447
0.6996	0.2006	0.79209	–0.593	–6.221	–0.486	0.3007	0.6001	0.84674	–0.693	–14.446	–0.518
0.6014	0.2984	0.80200	–0.624	–9.301	–0.476	0.2009	0.0988	0.79294	–0.093	16.411	–0.558
0.5014	0.3983	0.81512	–0.704	–12.213	–0.525	0.2031	0.3003	0.80408	–0.225	16.895	–0.605
0.5005	0.3000	0.80238	–0.498	–5.738	–0.398	0.1995	0.4009	0.81268	–0.314	13.031	–0.570
0.4983	0.2017	0.79378	–0.326	1.579	–0.359	0.2003	0.5006	0.82388	–0.387	6.273	–0.492
0.5012	0.0963	0.78696	–0.153	8.215	–0.347	0.1999	0.7001	0.86567	–0.588	–11.254	–4.666
0.4010	0.0955	0.78904	–0.123	12.457	–0.438	0.1004	0.1029	0.79499	–0.119	15.429	–0.580
0.4002	0.1992	0.79518	–0.267	7.740	–0.440	0.1032	0.2046	0.79909	–0.100	21.483	–0.676
0.3986	0.3022	0.80319	–0.401	1.000	–0.422	0.0986	0.3001	0.80476	–0.151	24.275	–0.736
0.4010	0.3988	0.81366	–0.547	–6.759	–0.438	0.0994	0.3996	0.81214	–0.198	23.872	–0.705
0.4005	0.4981	0.82979	–0.731	–14.159	–0.541	0.1479	0.0469	0.79142	–0.015	12.600	–0.402
0.3026	0.0958	0.79098	–0.102	15.300	–0.512	0.2520	0.0482	0.78961	–0.024	14.963	–0.457
0.2968	0.2023	0.79682	–0.212	13.688	–0.538	0.1500	0.8005	0.89779	–0.553	–11.840	–0.448
308.15 K											
0.8981	0.0523	0.77185	–0.143	0.475	–0.151	0.3000	0.3014	0.80376	–0.327	14.502	–0.625
0.0498	0.0458	0.79312	–0.037	11.613	–0.405	0.2871	0.4241	0.81553	–0.436	6.985	–0.556
0.8037	0.0947	0.77842	–0.248	0.416	–0.255	0.2992	0.4993	0.82605	–0.543	–1.117	–0.526
0.6996	0.2006	0.79209	–0.595	–2.397	–0.554	0.3007	0.6001	0.84674	–0.701	–10.881	–0.570
0.6014	0.2984	0.80200	–0.631	–5.318	–0.546	0.2009	0.0988	0.79294	–0.097	21.393	–0.693

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
0.5974	0.1010	0.78489	–0.191	8.563	–0.375	0.2008	0.1996	0.79795	–0.179	23.498	–0.766
0.5014	0.3983	0.81512	–0.712	–8.205	–0.592	0.2031	0.3003	0.80408	–0.234	22.153	–0.723
0.5005	0.3000	0.80238	–0.507	–0.790	–0.493	0.1995	0.4009	0.81268	–0.324	18.214	–0.675
0.4983	0.2017	0.79378	–0.331	6.968	–0.472	0.2003	0.5006	0.82388	–0.396	11.180	–0.579
0.5012	0.0963	0.78696	–0.156	13.708	–0.475	0.1999	0.7001	0.86567	–0.594	–8.154	–0.506
0.4010	0.0955	0.78904	–0.127	17.966	–0.573	0.1004	0.1029	0.79499	–0.124	19.952	–0.708
0.4002	0.1992	0.79518	–0.274	13.312	–0.565	0.1032	0.2046	0.79909	–0.109	26.203	–0.800
0.3986	0.3022	0.80319	–0.410	6.400	–0.530	0.0986	0.3001	0.80476	–0.160	29.076	–0.850
0.4010	0.3988	0.81366	–0.556	–1.851	–0.525	0.0994	0.3996	0.81214	–0.207	28.692	–0.807
0.4005	0.4981	0.82979	–0.739	–10.267	–0.602	0.1479	0.0469	0.79142	–0.015	17.216	–0.534
0.3026	0.0958	0.79098	–0.104	20.625	–0.647	0.2520	0.0482	0.78961	–0.024	20.010	–0.595
0.2968	0.2023	0.79682	–0.220	19.158	–0.668	0.1500	0.8005	0.89779	–0.558	–10.099	–0.469
305.65 K											
0.8981	0.0523	0.77185	–0.144	3.034	–0.199	0.3000	0.3014	0.80376	–0.337	19.997	–0.740
0.0498	0.0458	0.79312	–0.041	15.749	–0.531	0.2871	0.4241	0.81553	–0.446	12.180	–0.651
0.8037	0.0947	0.77842	–0.250	3.936	–0.322	0.2992	0.4993	0.82605	–0.553	3.606	–0.603
0.6996	0.2006	0.79209	–0.596	1.447	–0.619	0.3007	0.6001	0.84674	–0.709	7.298	–0.621
0.6014	0.2984	0.80200	–0.637	–1.314	–0.615	0.2009	0.0988	0.79294	–0.101	26.395	–0.826
0.5974	0.1010	0.78489	–0.195	13.808	–0.488	0.2008	0.1996	0.79795	–0.188	28.692	–0.894
0.5014	0.3983	0.81512	–0.719	–4.176	–0.657	0.2031	0.3003	0.80408	–0.245	27.434	–0.842
0.5005	0.3000	0.80238	–0.515	4.184	–0.585	0.1995	0.4009	0.81268	–0.334	23.420	–0.778
0.4983	0.2017	0.79378	–0.337	12.385	–0.584	0.2003	0.5006	0.82388	–0.406	16.109	–0.665
0.5012	0.0963	0.78696	–0.161	19.227	–0.601	0.1999	0.7001	0.86567	–0.602	–5.040	–0.546

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
0.4010	0.0955	0.78904	–0.131	23.500	–0.706	0.1004	0.1029	0.79499	–0.130	24.493	–0.836
0.4002	0.1992	0.79518	–0.281	18.909	–0.688	0.1032	0.2046	0.79909	–0.118	30.942	–0.923
0.3986	0.3022	0.80319	–0.418	11.827	–0.637	0.0986	0.3001	0.80476	–0.170	33.897	–0.963
0.4010	0.3988	0.81366	–0.565	3.082	–0.612	0.0994	0.3996	0.81214	–0.219	33.532	–0.910
0.4005	0.4981	0.82979	–0.747	–6.355	–0.662	0.1479	0.0469	0.79142	–0.018	21.850	–0.666
0.3026	0.0958	0.79098	–0.108	25.973	–0.782	0.2520	0.0482	0.78961	–0.028	25.079	–0.732
0.2968	0.2023	0.79682	–0.227	24.653	–0.795	0.1500	0.8005	0.89779	–0.564	–8.350	–0.490
303.15 K											
0.8981	0.0523	0.77185	–0.145	5.607	–0.245	0.3000	0.3014	0.80376	–0.346	25.518	–0.854
0.0498	0.0458	0.79312	–0.046	19.901	–0.656	0.2871	0.4241	0.81553	–0.457	17.400	–0.746
0.8037	0.0947	0.77842	–0.254	7.475	–0.389	0.2992	0.4993	0.82605	–0.563	8.352	–0.681
0.6996	0.2006	0.79209	–0.597	5.311	–0.684	0.3007	0.6001	0.84674	–0.718	–3.968	–0.671
0.6014	0.2984	0.80200	–0.644	2.712	–0.684	0.2009	0.0988	0.79294	–0.106	31.420	–0.957
0.5974	0.1010	078489	–0.200	19.078	–0.601	0.2008	0.1996	0.79795	–0.198	33.909	–1.021
0.5014	0.3983	0.81512	–0.726	–0.126	–0.722	0.2031	0.3003	0.80408	–0.256	32.739	–0.959
0.5005	0.3000	0.80238	–0.524	9.184	–0.678	0.1995	0.4009	0.81268	–0.345	28.650	–0.881
0.4983	0.2017	0.79378	–0.344	17.828	–0.695	0.2003	0.5006	0.82388	–0.416	21.060	–0.750
0.5012	0.0963	0.78969	–0.165	24.773	–0.725	0.1999	0.7001	0.86567	–0.610	–1.911	–0.587
0.4010	0.0955	0.78904	–0.137	29.060	–0.839	0.1004	0.1029	0.79499	–0.138	29.054	–0.963
0.4002	0.1992	0.79518	–0.288	24.534	–0.809	0.1032	0.2046	0.79909	–0.129	35.702	–1.045
0.3986	0.3022	0.80319	–0.427	17.280	–0.743	0.0986	0.3001	0.80476	–.0.181	38.738	–1.075
0.4010	0.3988	0.81366	–0.574	8.039	–0.698	0.0994	0.3996	0.81214	–0.231	38.393	–1.011
0.4005	0.4981	0.82979	–0.755	–2.422	–0.721	0.1479	0.0469	0.79142	–0.021	26.503	–0.796

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
0.3026	0.0958	0.79098	–0.113	31.346	–0.916	0.2520	0.0482	0.78961	–0.031	30.169	–0.868
0.2968	0.2023	0.79682	–0.236	30.174	–0.922	0.1500	0.8005	0.89779	–0.570	–6.594	–0.512
0.8981	0.0523	0.77185	–0.146	8.194	–0.291	0.3000	0.3014	0.80376	–0.356	31.063	–0.967
300.65 K											
0.0498	0.0458	0.79312	–0.050	24.068	–0.779	0.2871	0.4241	0.81553	–0.468	22.644	–0.840
0.8037	0.0947	0.77842	–0.258	11.033	–0.454	0.2992	0.4993	0.82605	–0.573	13.121	–0.757
0.6996	0.2006	0.79209	–0.600	9.195	–0.749	0.3007	0.6001	0.84674	–0.727	–0.079	–0.722
0.6014	0.2984	0.80200	–0.652	6.759	–0.752	0.2009	0.0988	0.79294	–0.112	36.464	–1.087
0.5974	0.1010	0.78489	–0.204	24.374	–0.710	0.2008	0.1996	0.79795	–0.208	39.148	–1.146
0.5014	0.3983	0.81512	–0.735	3.946	–0.787	0.2031	0.3003	0.80408	–0.267	38.066	–1.073
0.5005	0.3000	0.80238	–0.533	14.209	–0.768	0.1995	0.4009	0.81268	–0.357	33.903	–0.982
0.4983	0.2017	0.79378	–0.352	23.297	–0.804	0.2003	0.5006	0.82388	–0.427	26.032	–0.834
0.5012	0.0963	0.78696	–0.171	30.344	–0.849	0.1999	0.7001	0.86567	–0.618	1.232	–0.627
0.4010	0.0955	0.78904	–0.142	34.644	–0.968	0.1004	0.1029	0.79499	–0.146	33.632	–1.089
0.4002	0.1992	0.79518	–0.296	30.184	–0.929	0.1032	0.2046	0.79909	–0.140	40.479	–1.164
0.3986	0.3022	0.80319	–0.436	22.759	–0.848	0.0986	0.3001	0.80476	–0.193	43.599	–1.186
0.4010	0.3988	0.81366	–0.583	13.021	–0.782	0.0994	0.3996	0.81214	–0.242	43.272	–1.109
0.4005	0.4981	0.82979	–0.764	1.531	–0.780	0.1479	0.0469	0.79142	–0.023	31.173	–0.924
0.3026	0.0958	0.79098	–0.117	36.740	–1.047	0.2520	0.0482	0.78961	–0.035	35.280	–1.001
0.2968	0.2023	0.79682	–0.245	35.719	–1.047	0.1500	0.8005	0.89779	–0.577	–4.829	–0.533
298.15 K											
0.8981	0.0523	0.77185	–0.148	10.795	–0.337	0.3000	0.3014	0.80376	–0.366	36.634	–1.077
0.0498	0.0458	0.79312	–0.055	28.522	–0.899	0.2871	0.4241	0.81553	–0.479	27.913	–0.932

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
0.8037	0.0947	0.77842	–0.260	14.609	–0.518	0.2992	0.4993	0.82605	–0.583	17.912	–0.831
0.6996	0.2006	0.79209	–0.601	13.098	–0.813	0.3007	0.6001	0.84674	–0.736	3.557	–0.771
0.6014	0.2984	0.80200	–0.658	10.828	–0.819	0.2009	0.0988	0.79294	–0.118	41.529	–1.215
0.5974	0.1010	0.78489	–0.208	29.695	–0.818	0.2008	0.1996	0.79795	–0.218	44.410	–1.270
0.5014	0.3983	0.81512	–0.743	8.039	–0.850	0.2031	0.3003	0.80408	–0.278	43.416	–1.186
0.5005	0.3000	0.80239	–0.541	19.260	–0.856	0.1995	0.4009	0.81268	–0.367	39.178	–1.081
0.4983	0.2017	0.79378	–0.358	28.793	–0.911	0.2003	0.5006	0.82388	–0.438	31.027	–0.918
0.5012	0.0963	0.78696	–0.175	35.940	–0.969	0.1999	0.7001	0.86567	–0.627	4.390	–0.667
0.4010	0.0955	0.78904	–0.146	40.252	–1.095	0.1004	0.1029	0.79499	–0.153	38.228	–1.212
0.4002	0.1992	0.79518	–0.303	35.860	–1.047	0.1032	0.2046	0.79909	–0.150	45.277	–1.282
0.3986	0.3022	0.80319	–0.445	28.264	–0.951	0.0986	0.3001	0.80476	–0.204	48.480	–1.295
0.4010	0.3988	0.81366	–0.592	18.027	–0.865	0.0994	0.3996	0.81214	–0.253	48.171	–1.207
0.4005	0.4981	0.82979	–0.773	5.504	–0.838	0.1479	0.0469	0.79142	–0.026	35.862	–1.050
0.3026	0.0958	0.79098	–0.121	42.157	–1.176	0.2520	0.0482	0.78961	–0.038	40.411	–1.131
0.2968	0.2023	0.79682	–0.253	41.288	–1.169	0.1500	0.8005	0.89779	–0.584	–3.057	–0.555
295.65 K											
0.8981	0.0523	0.77185	–0.149	13.437	–0.380	0.3000	0.3014	0.80376	–0.375	42.228	–1.185
0.0498	0.0458	0.79312	–0.060	32.451	–1.018	0.2871	0.4241	0.81553	–0.490	33.205	–1.022
0.8037	0.0947	0.77842	–0.263	18.203	–0.581	0.2992	0.4993	0.82605	–0.593	22.726	–0.905
0.6996	0.2006	0.79209	–0.603	17.021	–0.875	0.3007	0.6001	0.84647	–0.746	7.212	–0.821
0.6014	0.2984	0.80200	–0.664	14.917	–0.884	0.2009	0.0988	0.79294	–0.123	46.613	–1.339
0.5974	0.1010	0.78489	–0.213	35.042	–0.924	0.2008	0.1996	0.79795	–0.228	49.693	–1.391
0.5014	0.3983	0.81512	–0.750	12.153	–0.913	0.2031	0.3003	0.80408	–0.288	48.788	–1.296

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
0.5005	0.3000	0.80238	–0.550	24.335	–0.944	0.1995	0.4009	0.81268	–0.377	44.474	–1.178
0.4983	0.2017	0.79378	–0.365	34.314	–1.016	0.2003	0.5006	0.82388	–0.448	36.042	–0.999
0.5012	0.0963	0.78696	–0.180	41.562	–1.087	0.1999	0.7001	0.86567	–0.635	7.562	–0.706
0.4010	0.0955	0.78904	–0.152	45.885	–1.221	0.1004	0.1029	0.79499	–0.159	42.841	–1.332
0.4002	0.1992	0.79518	–0.311	41.561	–1.162	0.1032	0.2046	0.79909	–0.160	50.093	–1.397
0.3986	0.3022	0.80319	–0.453	33.795	–1.051	0.0986	0.3001	0.80476	–0.215	53.379	–1.402
0.4010	0.3988	0.81366	–0.602	23.058	–0.947	0.0994	0.3996	0.81214	–0.265	53.090	–1.303
0.4005	0.4981	0.82979	–0.781	9.497	–0.895	0.1479	0.0469	0.79142	–0.030	40.570	–1.175
0.3026	0.0958	0.79098	–0.126	47.597	–1.303	0.2520	0.0482	0.78961	–0.041	45.564	–1.260
0.2968	0.2023	0.79682	–0.261	46.880	–1.289	0.1500	0.8005	0.89779	–0.592	–1.276	–0.577
293.15 K											
0.8981	0.0523	0.77185	–0.151	16.037	–0.425	0.3000	0.3014	0.80376	–0.385	47.849	–1.293
0.0498	0.0458	0.79312	–0.065	36.666	–1.135	0.2871	0.4241	0.81553	–0.501	38.520	–1.111
0.8037	0.0947	0.77842	–0.266	21.816	–0.643	0.2992	0.4993	0.82605	–0.603	27.562	–0.978
0.6996	0.2006	0.79209	–0.605	20.963	–0.936	0.3007	0.6001	0.84674	–0.755	10.884	–0.870
0.6014	0.2984	0.80200	–0.671	19.028	–0.948	0.2009	0.0988	0.79294	–0.129	51.720	–1.463
0.5974	0.1010	0.78489	–0.217	40.413	–1.028	0.2008	0.1996	0.79795	–0.238	54.998	–1.510
0.5014	0.3983	0.81512	–0.759	16.287	–0.974	0.2031	0.3003	0.80408	–0.299	54.185	–1.406
0.5005	0.3000	0.80238	–0.559	29.436	–1.031	0.1995	0.4009	0.81268	–0.389	49.794	–1.275
0.4983	0.2017	0.79378	–0.372	39.861	–1.120	0.2003	0.5006	0.82388	–0.459	41.089	–1.079
0.5012	0.0963	0.78696	–0.185	47.209	–1.203	0.1999	0.7001	0.86567	–0.645	10.749	–0.745
0.4010	0.0955	0.78904	–0.157	51.543	–1.344	0.1004	0.1029	0.79499	–0.167	47.474	–1.451
0.4002	0.1992	0.79518	–0.319	47.289	–1.277	0.1032	0.2046	0.79909	–0.170	54.929	–1.511

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
0.3986	0.3022	0.80319	–0.463	39.352	–1.152	0.0986	0.3001	0.80476	–0.227	58.298	–1.507
0.4010	0.3988	0.81366	–0.611	28.112	–1.027	0.0994	0.3996	0.81214	–0.276	58.029	–1.398
0.4005	0.4981	0.82979	–0.791	13.510	–0.952	0.1479	0.0469	0.79142	–0.033	45.295	–1.296
0.3026	0.0958	0.79098	–0.131	53.060	–1.428	0.2520	0.0482	0.78961	–0.045	50.737	–1.386
0.2968	0.2023	0.79682	–0.270	52.498	–1.408	0.1500	0.8005	0.89779	–0.600	0.512	–0.599
290.65 K											
0.8981	0.0523	0.77185	–0.152	18.678	–0.467	0.3000	0.3014	0.80376	–0.395	53.493	–1.398
0.0498	0.0458	0.79312	–0.069	40.895	–1.249	0.2871	0.4241	0.81553	–0.510	43.858	–1.198
0.8037	0.0947	0.77842	–0.267	25.446	–0.702	0.2992	0.4993	0.82605	–0.613	32.419	–1.049
0.6996	0.2006	0.79209	–0.605	24.924	–0.994	0.3007	0.6001	0.84674	–0.765	14.573	–0.918
0.6014	0.2984	0.80200	–0.678	23.159	–1.012	0.2009	0.0988	0.79294	–0.135	56.845	–1.584
0.5974	0.1010	0.78489	–0.221	45.809	–1.129	0.2008	0.1996	0.79795	–0.247	60.323	–1.626
0.5014	0.3983	0.81512	–0.766	20.442	–1.035	0.2031	0.3003	0.80408	–0.311	59.603	–1.514
0.5005	0.3000	0.80238	–0.566	34.599	–1.114	0.1995	0.4009	0.81268	–0.399	55.134	–1.368
0.4983	0.2017	0.79378	–0.379	45.434	–1.222	0.2003	0.5006	0.82388	–0.469	46.137	–1.158
0.5012	0.0963	0.78696	–0.188	52.881	–1.317	0.1999	0.7001	0.86567	–0.654	13.949	–0.784
0.4010	0.0955	0.78904	–0.160	57.222	–1.464	0.1004	0.1029	0.79499	–0.173	52.121	–1.567
0.4002	0.1992	0.79518	–0.326	53.041	–1.389	0.1032	0.2046	0.79909	–0.179	59.780	–1.621
0.3986	0.3022	0.80319	–0.471	44.932	–1.249	0.0986	0.3001	0.80476	–0.237	63.235	–1.610
0.4010	0.3988	0.81366	–0.620	33.190	–1.107	0.0994	0.3996	0.81214	–0.287	62.984	–1.490
0.4005	0.4981	0.82979	–0.800	17.543	–1.008	0.1479	0.0469	0.79142	–0.037	50.038	–1.417
0.3026	0.0958	0.79098	–0.136	58.544	–1.550	0.2520	0.0482	0.78961	–0.049	55.930	–1.510
0.2968	0.2023	0.79682	–0.278	58.138	–1.524	0.1500	0.8005	0.89779	–0.608	2.309	–0.621

TABLE II. Continued

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$10^6\alpha^E$ (K^{-1})	$(\partial H^E/\partial P)_T$ (JMPa^{-1} mol^{-1})
288.15 K											
0.8981	0.0523	0.77185	–0.199	21.366	–0.556	0.3000	0.3014	0.80376	–0.459	59.241	–1.556
0.0498	0.0458	0.79312	–0.161	45.203	–1.449	0.2871	0.4241	0.81553	–0.566	49.296	–1.329
0.8037	0.0947	0.77842	–0.319	29.141	–0.810	0.2992	0.4993	0.82605	–0.662	37.365	–1.159
0.6996	0.2006	0.79209	–0.651	28.951	–1.098	0.3007	0.6001	0.84674	–0.804	18.326	–0.995
0.6014	0.2984	0.80200	–0.724	27.357	–1.114	0.2009	0.0988	0.79294	–0.215	62.068	–1.778
0.5974	0.1010	0.78489	–0.282	51.301	–1.228	0.2008	0.1996	0.79795	–0.324	65.755	–1.808
0.5014	0.3983	0.81512	–0.811	24.664	–1.131	0.2031	0.3003	0.80408	–0.380	65.126	–1.679
0.5005	0.3000	0.80238	–0.619	39.770	–1.242	0.1995	0.4009	0.81268	–0.461	60.582	–1.513
0.4983	0.2017	0.79378	–0.438	51.104	–1.375	0.2003	0.5006	0.82388	–0.523	51.295	–1.279
0.5012	0.0963	0.78696	–0.255	58.656	–1.491	0.1999	0.7001	0.86567	–0.690	17.212	–0.850
0.4010	0.0955	0.78904	–0.232	63.009	–1.650	0.1004	0.1029	0.79499	–0.261	56.862	–1.762
0.4002	0.1992	0.79518	–0.392	58.898	–1.557	0.1032	0.2046	0.79909	–0.261	64.734	–1.803
0.3986	0.3022	0.80319	–0.530	50.612	–1.394	0.0986	0.3001	0.80476	–0.313	68.278	–1.776
0.4010	0.3988	0.81366	–0.670	38.354	–1.225	0.0994	0.3996	0.81214	–0.356	68.049	–1.639
0.4005	0.4981	0.82979	–0.842	21.641	–1.096	0.1479	0.0469	0.79142	–0.132	54.878	–1.627
0.3026	0.0958	0.79098	–0.211	64.131	–1.742	0.2520	0.0482	0.78961	–0.132	61.223	–1.711
0.2968	0.2023	0.79682	–0.347	63.883	–1.699	0.1500	0.8005	0.89779	–0.637	4.145	–0.664

$$\bar{V}_i^{\mathrm{E}} = V^{\mathrm{E}} + \left(\frac{\partial V^{\mathrm{E}}}{\partial x_i}\right)_{P,T,x_j,j\neq i} - \sum_{k=1}^{N} x_k \left(\frac{\partial V^{\mathrm{E}}}{\partial x_k}\right)_{P,T,x_j,j\neq k} \tag{11}$$

taking into account that the excess volumes have been correlated by Eq. (2), thus the parameters reported in Table III were used. The limiting pure partial excess molar volumes should be determined by considering infinite dilution in Eq. (11); such limiting values depend only on the correlation parameters. The values of the limiting pure partial excess molar volumes for the ternary system at different temperatures are given in Table IV. In this ternary system, it can be observed that for compositions rich in 1–pentanol, the magnitude of the partial excess volume decreases because of the strong effect of ethanol. This magnitude (positive limiting values) also decreases for higher temperatures. However, in the ethanol + water system, the opposite trend was observed, this magnitude is slightly dependent on temperature.

TABLE III. Parameters of Eq. (5) in the range 288.15 – 323.15 K and σ in accordance to Eq. (6)

$C_{00} = -8791.047$	$C_{01} = 83.660$	$C_{02} = -0.266$	$C_{03} = -4.068 \times 10^{-3}$	
$C_{10} = -3923.186$	$C_{11} = 40.779$	$C_{12} = -0.139$	$C_{13} = -3.344 \times 10^{-3}$	
$C_{20} = 11951.086$	$C_{21} = -114.193$	$C_{22} = 0.364$	$C_{23} = -3.761 \times 10^{-3}$	$\sigma = 0.038$

TABLE IV. Partial excess molar volumes at infinite dilution of the binary mixtures in the temperature range 288.15 – 323.15 K

Mixture	$\bar{V}_1^{\mathrm{E},\infty}$ (cm^3 mol^{-1})	$\bar{V}_2^{\mathrm{E},\infty}$ (cm^3 mol^{-1})
288.15 K		
Ethanol + water	–4.84	–2.39
Ethanol + 1-pentanol	0.33	0.74
293.15 K		
Ethanol + water	–4.98	–2.45
Ethanol + 1-pentanol	0.32	0.74
298.15 K		
Ethanol + water	–5.12	–2.49
Ethanol + 1-pentanol	0.30	0.71
308.15 K		
Ethanol + water	–5.31	–2.56
Ethanol + 1-pentanol	0.30	0.69
323.15 K		
Ethanol + water	–5.58	–2.46
Ethanol + 1-pentanol	0.32	0.71

EQUATIONS OF STATE FOR EXCESS MOLAR VOLUMES

In the last few years, interest in equations of state for the correlation and prediction of thermodynamic properties (excess molar volumes, partial excess and partial molar volumes, phase equilibria, excess molar ethalpies, *etc.*) has increased. This fact is due to their simplicity as models, low data requirements and versatility in operational conditions. A considerable number of equations of state are available in the literature, most of them being adequate to obtain acceptable results by simple rules if the parameters are obtained from binary mixtures encompassed in multicomponent system. In this case, the Soave–Redlich–Kwong (SRK) equation was applied to a and b. For a binary mixture, at constant p and T, the excess molar volume is expressed as follows:

$$V^{\mathrm{E}} = \Delta V = V_{\mathrm{m}} - \sum_{i=1}^{n} x_i V_i = \sum_{i=1}^{n} x_i \left(-\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_{j\neq i}} \left(\frac{\partial p}{\partial V}\right)_{T,n_i}^{-1} - V_i \right) \quad (12)$$

where the partial derivatives and the molar volume are obtained from the selected equation of state. The parameters a and b are given by the following mixing rules:

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (1 - k_{ij} - l_{ij} z)(a_i a_j)^{0.5} \quad (13)$$

$$b = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (1 - m_{ij}) \left(\frac{b_i + b_j}{2} \right) \quad (14)$$

$$\text{Mixing rule R1: } l_{ij} = m_{ij} = 0 \quad (15)$$

$$\text{Mixing rule R2: } l_{ij} = 0 \quad (16)$$

$$\text{Mixing rule R3: } k_{ij}, l_{ij}, m_{ij} \neq 0 \quad (17)$$

where the parameters (k_{ij}, l_{ij} and m_{ij}) are constant values over the whole composition diagrams for each binary mixture and where $z = (x_i - x_j)$. A Marquardt[7] non-linear algorithm was used to compute the parameters. The accuracy of the different mixing rules are shown in Fig. 5 for the binary ethanol + 1-pentanol at 298.15 K.

Despite of this, accuracy of the correlation of the experimental data, prediction of the ternary values fails mainly due to two facts: firstly the liquid-liquid split in the proximity of the binary water + 1-pentanol leads us to apply only the binary parameters of the equation of state corresponding to the other homogeneous binaries contained in the ternary mixture; secondly, the huge ternary contributions (Fig. 2), which is not taken into account in the ternary prediction (more than 50 % sometimes) produce inaccuracies in the calculations at each temperature. These two

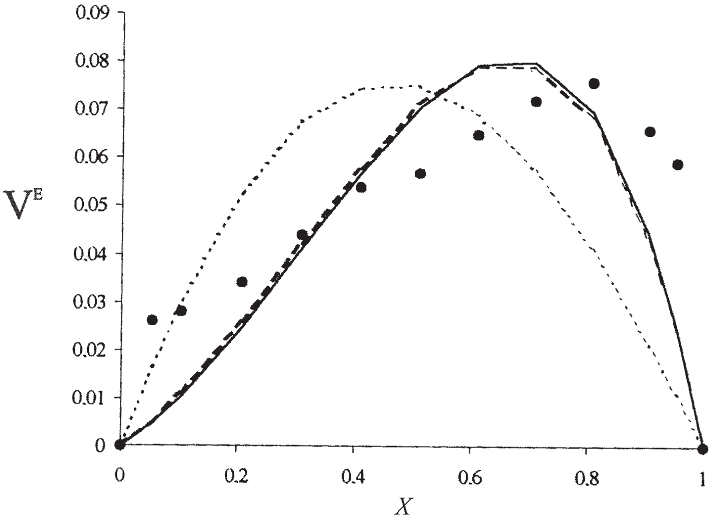

FIG. 5. Comparison of the experimental excess molar volumes ($cm^3 \, mol^{-1}$) and fitted by SRK equation of state with different mixing rules, (•) experimental data for ethanol (1) + 1-pentanol (3), (——-) R1, (– – –) R2 and (····) R3 at 298.15 K.[4]

facts lead to strong understimations of the negative excess molar volumes and high deviations for all mixing rules. The necessary data for the calculations were taken from the open literature (Table V).

TABLE V. Open literature and estimated critical values for the compounds included in the ternary mixture

Compound	P_c/bar	T_c/K	Z_c	ω
Ethanol	61.48	513,92	0.240	0.649
Water	220.64	647.14	0.229	0.344
1-Pentanol	39.09	588.15	0.262	0.579

In general, excess volumes depend mainly on two effects: a) the variation of the intermolecular forces when two components come into contact and b) the variation of the molecular packing as a consequence of the differences in the size and shape of the molecules of the components. In ternary systems, complex interactions occur, steric hindrance and geometrical factors being of key importance to the understanding and prediction of excess magnitude of the multicomponent. In the studied system, the intermolecular associations *via* H-bonding by ethanol and water, were also observed for 1-pentanol, which shows relative hindrance and slightly polar interactions due to the hydroxyl group being partially deactivated. Ternary contribution of a different character attaining to the 1-pentanol composition is the cause of the observed huge negative values around the equimolar pseudobinary ethanol + water system; this packing, not surprisingly is sensitive to the temperature, a diminution of this attraction being noted when the temperature increases. The liquid-liquid split observed (around water + 1-pentanol compositions) agree with this interpretation; a diminution of the ethanol content destroy the tridimensional structure of the polar molecules and produces a separation into an aqueous and an organic phase.

In Figs. 1 and 2, the split zone is of slightly positive excess molar volumes or low negative values, although it is not encompassed. The opposite role of the short hydroxylated solvents and 1-pentanol is clearly noted by means of the data given in Table IV, where the limiting partial excess molar volumes are shown. Strong positive values were computed for the binary ethanol + 1-pentanol, in both cases with a slight dependence on temperature. The analysis of excess expansibility and isothermal coefficient of pressure excess molar enthalpy reveled a higher sensitivity of the pseudobinary of ethanol + water with temperature and a change in the slope of the derivation of the excess molar enthalpy as a function of temperature.

As commented above, despite accurate descriptions of the binary mixtures by the equation of state (see Fig. 5 for the binary ethanol + 1-pentanol), a low capability for prediction was obtained, due to the huge ternary contribution with respect to the total value of the excess molar volume and the lack of parameters for the binary water + 1-pentanol. According to the obtained results, it is necessary to apply more robust mixing rules (non-quadratic, excess Gibbs energy dependent rules, *etc*.) for a description of these complex systems (high non ideality, phase split, *etc*), poor predicting results being obtained when the interactions among the three different molecules take place, due to this approximation not being considered in the structure of the applied combination mixing rules. The important non-ideality and the considerable ternary contribution support the idea that similar effects will be observed when the addition of other key components is made to mixtures containing ethanol and water. This intense interaction produces large deviations from ideality resulting in great difficulties during modelling and simulation. Nowadays, the implementation of adequate mixing rules and a suitable description of the temperature dependence attractive term ($\alpha(T)$) parameter for partially miscible, highly-non ideal multicomponent mixtures is being studied in our laboratory for application to high order multicomponent cases, which are related to mixtures of ethanol + water + key components (congeners), of interest in studies of the distillation of alcoholic beverages.

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ИЗВОД

УТИЦАЈ ТЕМПЕРАТУРЕ НА ЗАПРЕМИНСКЕ ОСОБИНЕ СМЕША ЕТАНОЛ + ВОДА + 1-ПЕНТАНОЛ

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Познавање физичких особина и фазних равнотежа неопходно је при пројектовању и оптимизацији опреме за производњу дестилованих алкохолних пића. У овом раду приказане су температурне зависности повећања моларне запремине тернерних система етанол + вода + 1-пентанол у температурном опсегу 288,15 – 323,15 K и атмосферском притиску, због улоге 1-пентанола као побољшивача укуса у тим пићима. Повећање моларне запремине је негативно у целој хомогеној области састава, али тежи ка позитивним вредностима у области бинарних смеша етанол+1-пентанол и вода+1-пентанол. Како је пројектовање процеса углавном компјутеризовано размотрено је колико су предвиђања на основу SRK једначине прецизна. Израчунате су различите изведене особине због значаја у проучавању специфичних међумолекулских интеракција.

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